Flavor Reversion in Soybean Oil. IV. Isolation of Reversion Compounds in Soybean Oil[1,2,3]

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Introduction

THE cause of flavor reversion in soybean oil has been a perplexing problem in the edible fat and oil industry for many years. However, on the basis of a great variety of experimental investigations, a number of hypotheses have been advanced to explain the development of objectionable flavors and odors in oils.

Durkee (1) has suggested that linolenic acid is responsible in some manner for reversion in unhardened soybean oil because of "the presence of three highly reactive double bonds." Support for this idea has been found in the fact that oils which revert easily contain considerable quantities of linolenic acid. Studies by Lemon (2, 3) on hydrogenated oils have shown the presence of isolinoleic acids, the disappearance of which coincided with the disappearance of flavor reversion.

Although much of the work concerning precursors has been centered about linolenic acid, investigations into other possibilities are currently in progress. Mattil (4) has recently reported that the unsaponifiable fraction may have a role in soybean oil reversion. Goss (5), after conducting a survey of the German oil processing industries, has stated that German technologists have attributed reversion to the presence of lecithin in oils, and have succeeded in improving flavor quality by its removal. Dutton, Moser, and Cowan (6) extended the water-washing process for the removal of lecithin by treatment with a small amount of citric acid during deodorization. The resulting oil "possessed a significantly higher flavor stability" than oil refined according to conventional processes.

As cited in previous papers from this laboratory, our approach to the problem of reversion was made with no *a priori* opinions as to the causative nature of reversion in soybean oil. This paper deals with the isolation of compounds that contribute to the reverted flavor in soybean oil.

Experimental

The oils employed in this work were of commercial, alkali-refined grade and consisted of hardened (I.V. = 103) and unhardened (I.V. = 136) soybean oils.*

Organoleptic Analysis. Organoleptic detection of reverted flavors was conducted with a panel of five well-trained individuals according to the procedure adopted at the Northern Regional Research Laboratory (7). Flavor tests were made on a comparative basis and no more than two samples were compared at any one time. Samples with highly reverted flavors were usually diluted with mineral oil to a concentration approximating that found in the original soybean oil.

Reversion and Deodorization. The off-flavors present in reverted soybean oil were removed by steam deodorization for one hour at 200°C. and 1-2 mm. pressure, using the apparatus designed by Bailey and Feuge (8). To obtain a large number of condensates the oils were successively heat-reverted by heating to 200°C. and then cooled rapidly, followed by steam deodorization.

One and a half kilos of hardened and unhardened soybean oils were subjected to 40 successive operations of heat reversion and deodorization. The total condensate in each case was extracted with ethyl ether (Figure 1). The ether-soluble fraction has been investigated in this laboratory by Golumbic, Martin, and Daubert (9). This fraction exhibited selective absorption in the ultraviolet region at 264-268 mμ in isooctane solution. In an attempt at concentration of the "reversion compounds" the sterol portion of a similar fraction was removed by low-temperature crystallization in acetone, and the remaining material investigated by chromatographic adsorption. None of the fractions examined imparted a definite reverted flavor to bland soybean oil. This led to the supposition that the "reversion compounds" were volatile and had been lost in their treatment of the ether-soluble fraction (9).

Vacuum Distillation of the Ether-Soluble Fraction. The volatility of the "reversion compounds" led to the adoption of the procedure of vacuum distillation at room temperature as a means of further concentration. The ether-soluble fraction was subjected to a high vacuum distillation with the volatile compo-

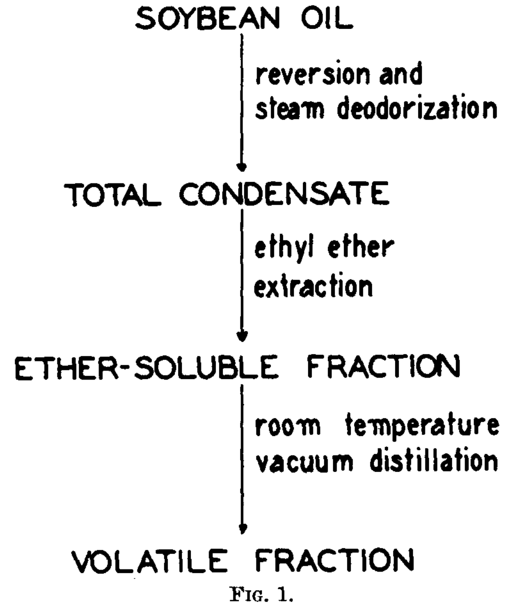

FIG. 1.

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[2] The generous financial assistance of the National Association of Margarine Manufacturers is gratefully acknowledged.

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*All tests and procedures mentioned are understood to have been conducted on both oils unless otherwise noted.

nents being trapped in a dry-ice condenser. Agitation was produced by a magnetic stirrer. Distillation under these conditions for a period of 10 hours was found sufficient to remove all of the volatile material (Fig. 1).

Spectrophotometric analysis of this volatile fraction was accomplished using a Beckman Model DU quartz spectrophotometer. The specific extinction values obtained were 93.3 and 27.6 at 262-3 mμ for the unhardened and hardened oils, respectively (Fig. 2),

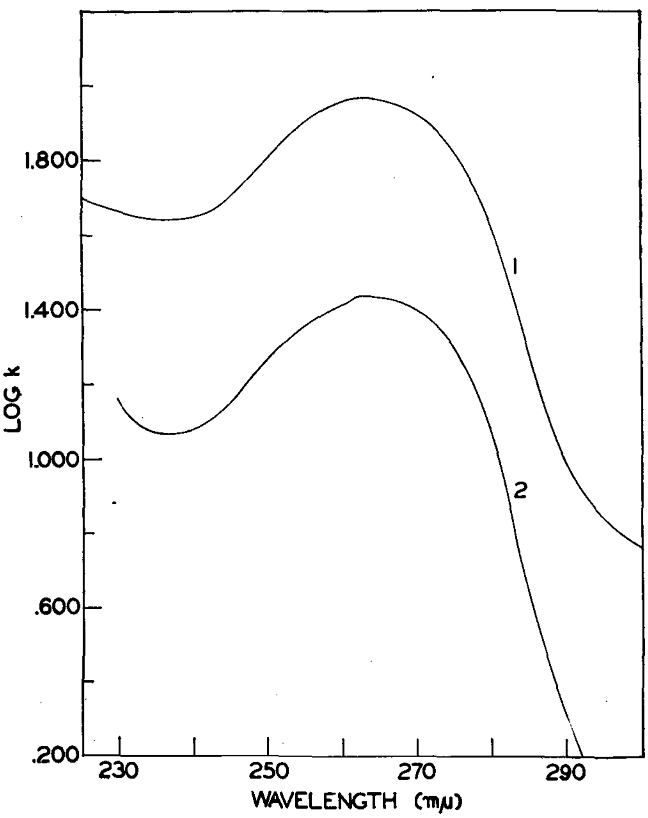

FIG. 2. Absorption Spectrum of Volatile Fraction

1. Unhardened soybean oil
2. Hardened soybean oil.

Micro Qualitative Analysis. Due to the small amount of volatile fraction available, organic qualitative analyses were conducted on a micro scale. Positive tests for aldehydes were obtained with Tollens' and Fuchsin reagents. Reaction with sodium bisulfite succeeded in removing almost all of the flavor materials from solution, but attempts at regeneration from the bisulfite complex failed.

Reaction with semicarbazide-HCl gave a product which had no definite melting point and showed extreme insolubility. The non-carbonyl residue upon reconstitution in mineral oil exhibited no typical reversion flavor. The crude semicarbazones were hydrolyzed with oxalic acid and the regenerated carbonyls, when reconstituted in mineral oil, gave a flavor similar to reverted soybean oil.

Reaction With Girard Reagent-T. A portion of the volatile fraction (100 mg.) was treated with 184 mg. of Girard's reagent-T (trimethylaminoacetohydrazine chloride) according to the method of Reichstein (10). The carbonyl-Girard complex was hydrolyzed to yield carbonyl fractions of 33.3 and 31.6 mg. for the unhardened and hardened oils, respectively. Organoleptic tests gave results similar to those obtained with semicarbazide; the carbonyl portion had a flavor similar to reverted soybean oil. On the basis of the amount of carbonyl material obtained by this method a calculation of the concentration of carbonyls in the original oil was made (Table I).

TABLE I

Concentration of Carbonyl Material in Soybean Oils

Type of Oil	Weight of Oil (g.)	Number of Reversions and Deodorizations	Weight of Ether-Soluble Fraction (g.)	Weight of Volatile Fraction (g.)	% Carbonyl in Volatile Fraction	% Carbonyl in Original Oil
Unhardened........	1500	40	7.716	0.829	33.3	.000458
Hardened............	1500	40	6.517	1.078	31.6	.000568

Preparation of 2,4-dinitrophenylhydrazones. The reaction of 2,4-dinitrophenylhydrazine and the carbonyl fraction obtained by the Girard reaction yielded an oil which could not be crystallized. Accordingly, the original volatile fraction was used in the following procedure.

Five hundred mg. of volatile fraction were dissolved in 66 ml. of ethyl alcohol, 910 mg. of 2,4-dinitrophenylhydrazine added, and the mixture was heated to boiling. Immediately following the addition of 2 ml. of concentrated HCl, a dark, insoluble precipitate formed. The reaction mixture was then refluxed gently for seven minutes. (Prolonged refluxing and the use of a clay chip result in oil formation.)

The highly insoluble precipitate was removed by filtration from the boiling alcoholic solution, yielding 25 mg. in the case of the unhardened oil (Compound A) and 5 mg. in the case of the hardened oil (Compound B) (Table II).

Attempts to purify these hydrazones were unsuccessful because of the meager quantities on hand and their very sparing solubility in alcohol and non-polar solvents. This prevented their purification by chromatographic analysis. They were found to be soluble, however, in hot nitrobenzene. Dicarbonyl structures have been ascribed tentatively to these impure derivatives on the basis of their extremely high melting points (295° and 290° for Compounds A and B, respectively) and the formation of a blue color with alcoholic KOH (11).

The mother liquor was allowed to cool to room temperature and another precipitate removed. Further cooling resulted in a number of such precipitates. These *soluble* precipitates were subjected to a series of some 25-30 recrystallizations from alcohol, resulting in the isolation of two clearly defined fractions: one was found to be excess reagent, the other a non-crystalline, red-orange powder melting at 114-115°C. (Compound C) for the unhardened oil, and at 109-110°C. (Compound D) for the hardened oil. These two derivatives were chromatographed and recrystallized until constant melting points were obtained.

Chromatography of Compounds C and D. The chromatography was conducted on columns 45 x 1.2 cm. using an adsorbent of powdered talc and Super-cel in a ratio of 1:1.5 by weight. The columns were packed with a slurry of the adsorbent in heptane which was also used as the solvent for the hydrazones.

For the chromatography of Compound C the separation of the bands was effected by a mixed solvent

TABLE II

2,4-Dinitrophenylhydrazones Obtained From Soybean Oil Aldehydes

Source of Aldehyde	Derivative	Weight (mg.)	Description	Melting Point (°C.)	Analyses			Empirical Formula
					C	H	N	
Unhardened Oil	A	25*	Red-Brown Powder	295	44.25	2.28	23.48	....
	C	20	Red-Orange Needles	122-123	53.87	4.97	18.90	$C_7H_{10-12}O$†
Hardened Oil	B	5*	Red Powder	290	43.70	3.26	24.10	....
	D	10	Red-Orange Needles	114-115	54.36	5.26	19.50	$C_7H_{10-12}O$†

* Crude precipitate weight.

† The formula $C_7H_{11}O$ obtained by calculation was found to be impossible.

containing 95% low-boiling petroleum ether (b.p. 35-40°) and 5% benzene. After development, there were two distinct bands—a light orange Band I (0.5 cm.) at the top of the column, and about half way down the column an orange-yellow Band II (13 cm.). This second band was eluted into the percolate with a mixture of 85% petroleum ether, 10% ethyl ether, and 5% benzene. Band I was eluted with ethyl ether and was found to contain excess reagent (2,4-dinitrophenylhydrazine). The material from Band II, eluted into the percolate, was Compound C.

For the chromatography of Compound D the separation of the bands was effected by a 1:1 mixture of petroleum ether and ethyl ether. An orange band (0.5 cm.) remained at the top of the column while a wide yellow band (20 cm.) moved rapidly down the column. The yellow band on the adsorbent was eluted with the same mixture of solvents; it contained Compound D. The orange band was eluted with ethyl ether; it contained 2,4-dinitrophenylhydrazine.

In the continuation of the purification of Compound C the material from Band II was taken up in 3 ml. of boiling ethyl alcohol and allowed to cool. The crystals obtained were light red needles; m.p. 119.6-120.2°C. This was recrystallized three times in ethyl alcohol; yield, 20.1 mg.; m.p. 122.3-123° C.; crystalline form, red-orange needles.

Analysis: C, 53.87; H, 4.97; N, 18.90%.

The chromatographed Compound D was purified in an analogous manner by two recrystallizations from ethyl alcohol; yield, 10 mg.; m.p. 114-115°C.; crystalline form, red-orange needles. (See Table II.)

Analysis: C, 54.36; H, 5.26; N, 19.50%.

The absorption spectra of the two crystalline derivatives, D and C, showed a maximum at 377-378 mμ and 385 mμ for the hardened and unhardened oils, respectively. The extinction coefficient, *k*, for Compound C was 111.5 (Table III).

Since oxidation with potassium permanganate, as well as a consideration of the empirical formulas (Table II) indicated unsaturation in the carbon chain of the derivatives, hydrogenation was selected as the next procedure.

Hydrogenation of Compound C. Ten milligrams of Compound C were dissolved in 15 ml. of purified ethyl acetate and 10 mg. of palladium on barium sulfate were added. The hydrogenation was carried out at room temperature and atmospheric pressure, with agitation effected by a magnetic stirrer. In approximately 45 minutes the uptake of hydrogen was complete, with the total uptake being 0.87 ml.

The hydrogenated products were chromatographed on the column previously described with powdered talc and Supercel in a ratio of 1:1 by weight. Heptane was used as the solvent and also as the developing agent. After development, three distinct bands were evident on the column. A light red-brown Band I (0.8 cm.) at the top of the column, a light violet Band II (8 cm.) in the middle and a yellow Band III (12 cm.) in the lower half of the column. Band III was eluted with low-boiling petroleum ether, the solvent removed, and the product crystallized from ethyl alcohol; m.p. 81-83°C. Three recrystallizations from ethyl alcohol gave a constant melting compound; yield, 2 mg.; m.p. 94-95°C.; crystalline form, yellow needles. The material in Bands I and II were too small in quantity for workability.

The absorption spectrum of the hydrogenated Compound C showed a maximum at 361 mμ, identical with the maximum for *n*-heptaldehyde-2,4-dinitrophenylhydrazone. A mixed melting point from an evaporated solution of the two gave m.p. 95-97°.

These results suggested that Compounds C and D were unsaturated seven-carbon aldehydes, i.e., heptenals. The α,β-unsaturation was chosen because of the color of the derivative, position of the absorption maximum (12), and the sodium bisulfite test (13).

Synthesis of α-Heptenal. Ethyl α-heptenoate (I) was prepared by the condensation of ethyl hydrogen malonate and *n*-valeraldehyde by the method of Galat

TABLE III

Comparison of 2,4-Dinitrophenylhydrazones

Source of Aldehyde	M.P. (°C.)	Color	λ of Max. Absorption (mμ)	Specific Extinction Coefficient k	X-ray Long Spacing (Å)	Analyses		
						C	H	N
Synthetic α-Heptenal	123-124	R.O.	377-378	96.9	17.1	53.43 53.42*	5.85 5.48*	19.15 19.18*
Unhardened Oil (Compound C)	122-123	R.O.	385	111.5	17.1	53.87	4.97	18.90
Hardened Oil (Compound D)	114-115	R.O.	377-378	......	17.8	54.36	5.26	19.50

* Indicates theoretical values.

(14). The ester was saponified with alcoholic potassium hydroxide and the potassium salt hydrolyzed with hydrochloric acid to give the α-heptenoic acid (II). α-Heptenoyl chloride (III) was prepared by the acylation of (II) with thionyl chloride (purified by distillation from quinoline followed by distillation from linseed oil). (III) was converted to α-heptenal (IV) by the Rosenmund reaction (15), employing toluene as the solvent and palladium on barium sulfate, poisoned with Quinoline-S.

The constants for α-heptenal were: b.p.$_{(106\text{ mm.})}$, 90-92° C.; $[n]^D_{20} = 1.4418$, $[n]^D_7 = 1.4470$; semicarbazone, 167-168° C.; *p*-nitrophenylhydrazone, 110.5-111.5° C.; 2,4-dinitrophenylhydrazone, 123.4-124.2° C.

Delaby and Guillot-Allégre (16), employing a different synthesis, found: b.p.$_{(760\text{ mm.})}$, 165-167°C.; $[n]^D_7 = 1.4468$; semicarbazone, 169° C.; *p*-nitrophenylhydrazone, 110-112°C.

Analysis of the 2,4-dinitrophenylhydrazone gave: C, 53.43; H, 5.85; N, 19.15%. Calculated: C, 53.42; H, 5.48; N, 19.18.

The absorption spectrum of α-heptenal in isooctane showed no maxima between 220 and 320 mμ. The absorption spectrum of α-heptenal-2,4-dinitrophenylhydrazone showed a maximum at 378 mμ, $k = 96.6$.

An X-ray diffraction pattern showed a long-spacing value of 17.1 Å. Compounds C and D gave long-spacing values of 17.1 and 17.8 Å, respectively (Table III).

Discussion

It has been shown by many workers that steam deodorization will produce an oil that is entirely bland. Accordingly, as the first step in the isolation of the "reversion compounds" from reverted soybean oil, the off-flavors were removed by steam deodorization *in vacuo*. When the ether-soluble fraction of the total condensate was added back to the deodorized soybean oil, the reconstituted product had a fishy or painty flavor typical of heat-reverted soybean oil. Although it is not wholly certain that these flavors are identical with those initially present, nonetheless the observations indicate that the substances causing the reverted flavor may be removed unchanged, at least in part, by steam distillation *in vacuo*.

The ether-soluble fraction was used in this study for it was definitely established that the ether-soluble fraction, and not the water fraction, contained the flavor constituents.

As already mentioned, the volatile material removed from the ether-soluble fraction had a higher specific extinction coefficient in the case of the unhardened soybean oil (Fig. 2). This does not necessarily imply that the concentration of "reversion compounds" is greater in the unhardened oil for it has not been possible, as yet, to associate this absorption peak with the presence of flavor constituents. It may be possible, however, that in future work this may provide an excellent criterion for the degree of reversion of an oil if a correlation can be made between the extinction at 262-263 mμ and the concentration of "reversion compounds."

Of the various qualitative tests conducted on the volatile material, the reactions with carbonyl reagents that permit regeneration were the most enlightening. Semicarbazide hydrochloride and Girard reagent-T gave products that were easily regenerated to give the carbonyl flavor materials. But the sodium bisulfite addition complex could not be hydrolyzed to compounds that gave a reverted flavor to a bland oil. This implied that the carbonyl material present in the volatile fraction imparted the reversion flavor to soybean oil and that this material, at least in part, was probably α,β-unsaturated (α-heptenal). Such a conclusion is plausible for α,β-unsaturated carbonyls are known to form non-hydrolyzable complexes with such reagents (13).

The purification of the 2,4-dinitrophenylhydrazones was best effected by chromatography. An extended series of fractional crystallizations did not produce well-defined crystalline forms but only amorphous powders. However, as few as one or two passages through a chromatographic column produced excellent crystalline structures and constant melting points. A comparison of the purified derivatives C and D with that of α-heptenal is given in Table III.

It is obvious from these data that the 2,4-dinitrophenylhydrazone obtained from the two oils are quite similar to the 2,4-dinitrophenylhydrazone of the synthetic α-heptenal. The discrepancies in the melting point and long-spacing value of the derivative from the hardened oil (Compound D) may be due to a difference in the stereochemical configuration about the double bonds. Further proof of the presence of α-heptenal in reverted soybean oil will be dependent on the formation of other derivatives.

Therefore, on the basis of evidence presented, it appears that α-heptenal may be one of the flavor components in reverted soybean oil. However, at this time no definite statement can be made regarding its contribution to reverted flavor for, when synthetic α-heptenal was added to bland soybean oil, it was difficult to assess the flavor of the reconstituted oil in terms of typical reverted soybean oil. A true assessment of its contribution to reversion may be made only when all of the "reversion compounds" have been identified.

A suggested precursor of α-heptenal in soybean oil is a conjugated triene of the eleostearic type with double bond conjugation in the 9,10, 11,12, and 13,14 positions; oxidation at the 11,12 position could produce the α,β-unsaturated aldehyde, α-heptenal. It is possible that the bond structure necessary for such a reaction to occur may result from the isomerization of linolenic acid.

"Reversion compounds" have been found in the condensate obtained from the deodorization of soybean oils. This condensate, when added to the bland oil, produced a flavor similar to that of reverted soybean oil.

The reversion flavors were found to disappear from the condensate when it was subjected to reduced pressure at room temperature. Advantage was taken of the high volatility to further concentrate the "reversion compounds." The compounds were vacuum distilled at room temperature and collected in a dry-ice trap. The volatile fraction gave a strongly reverted flavor when reconstituted in a bland oil.

Qualitative tests on the volatile fraction showed the presence of carbonyl compounds. The carbonyl constituents were separated from the non-carbonyl fraction by reaction with Girard reagent-T. The carbonyl portion possessed a flavor very similar to reverted soybean oil.

Two distinct 2,4-dinitrophenylhydrazones have been isolated from the carbonyl portions of both the hardened and unhardened soybean oils. The structure of the lower melting derivative, in each case, has been shown to correspond closely to the structure of α-heptenal.

Conjugated triene is suggested as a precursor to the formation of α-heptenal in reverted soybean oil.

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Adsorption Analysis of Lipids. II. The Fractionation of Soybean Oil and Derived Ethyl Esters[1]

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THE desire to fractionate glycerides of soybean oil arises from the need for a stable edible oil of low iodine value and a rapid-drying paint oil of high iodine value. Among the various methods of fractionation that have been employed are molecular distillation, low-temperature crystallization, and countercurrent extraction.

The molecular distillation process has been of little value in fractionating soybean glycerides with regard to unsaturation. A spread of 13.5 units in iodine value (126.6-139.1) is the maximum reported (1).

Fractional crystallization is more effective. By repeated recrystallization from acetone Bull and Wheeler (2) were able to obtain fractions as high in value as 166.1 and as low as 84.7, or a spread of 81.3 units. Golumbic, Martin, and Daubert (3) report a fractionation in which 16.7% of the total oil had an iodine value of 160.3; another fraction containing 25% of unsaponifiable matter comprising 0.9% of the total oil had an iodine value of 196.0. In a study of the component glycerides of soybean oil, Hilditch, Meara, and Holmberg (4) describe fractions ranging in iodine value from 114.3 to 163.7 and in linolenic acid content from 6.4 to 17.7%.

Extraction processes have given fractionations comparable or superior to those of fractional crystallization. The Solexol process (5), which uses propane as the solvent, is reported to fractionate oil yielding 30% of oil with an iodine value of 162 and 67.5% with an iodine value of 125. Using a two-solvent system of furfural and naphtha in a 50-foot countercurrent extraction column, Goss (6) reports iodine values of 116 to 173. Employing the same solvents in an 87-foot column, Gloyer (7) obtains a raffinate fraction comprising 30.1% with an iodine value of 95.5 and an extract fraction comprising 69.9% with an iodine value of 153.2.

No attempts to fractionate the glycerides of soybean oil by means of (chromatographic) adsorption analysis have been reported to date. However, Walker and Mills (8) applied this method to linseed oil and, using a single column, were able to separate fractions which had iodine values ranging from 116.2 to 202.8. Repeated adsorptions yielded fractions having iodine values of 117.7 to 246.5.

In the present study soybean glycerides and the mixed ethyl esters of soybean oil have been fractionated by adsorption on columns of aluminum oxide. These fractions were analyzed for fat acid composition by use of spectrophotometric and iodine value data. Total pigments, fraction weights, and the position of pigment bands were also measured. The utility of the adsorption column for the fractionation of glycerides of soybean oil and its ethyl esters is illustrated by the data presented.

Materials

The soybean oil used in these studies was a sample of commercially-produced, crude, degummed oil, extracted and stripped of solvent under mild temperature conditions. The ethyl esters used were prepared from this oil by trans-esterification with ethanol with use of sodium hydroxide as catalyst. The esters were extracted with petroleum ether, washed, dried, and stripped of solvent at 100°C. and then purified further by distillation at a pressure of 1 mm. and a temperature of 158°C., no attempt being made to fractionate them at this point. The iodine value of the crude oil was 134.2, that of the esters 125.8. Spectrophotometric analysis of the oil showed 8.1% linolenic acid, 52.7% linoleic acid, 26.2% oleic, and 13.0% saturated acids present as triglycerides.

The adsorbent used for this work was aluminum oxide, Harshaw's Al-2 powder.* This grade was selected after testing several brands for filtration

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[2] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

* The mention of this product does not imply that it is endorsed or recommended by the Department of Agriculture over others of a similar nature not mentioned.